Supporting Information

Near infrared spectra of high-density crystalline H_2O ices II, IV, V, VI, IX & XII

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Figure S1: Powder X-ray diffractograms (XRD) of all high-pressure ice samples using Cu $K_{\alpha 1}$ radiation (wavelength: 1.5406 Å). Each pattern represents a single scan of a given ice polymorph, so that each panel allows to judge on reproducibility. Reference diffractograms (bottom row of each panel) are calculated from published neutron or X-ray data for ices II (ref. 30), IV (ref. 31), V (ref. 32), VI (ref. 33), IX (ref. 34) and XII (ref. 35) using crystallography data analysis software GSAS-II. Slight shifts of Bragg peaks compared to literature data stem from different T-p conditions. While diffractograms shown in this study were measured at 77 K and subambient pressure (~ 10 Pa), the literature data were collected at different conditions (ice II: 110 K/ambient pressure, ice IV: 210 K/0.7 GPa, ice V: 98 K/ambient pressure, ice VI: 225 K/1.1 GPa, ice IX: 110 K/ambient pressure, ice XII: 260 K/0.5 GPa). Signals resulting from the Cu and Cu/Ni sample holders are marked with vertical lines and asterisks. The ice IV samples contain minor amounts of ice XII since both reaction channels, the formation of ice IV and the formation of ice XII, are operative upon heating uHDA at 0.8 GPa [36].

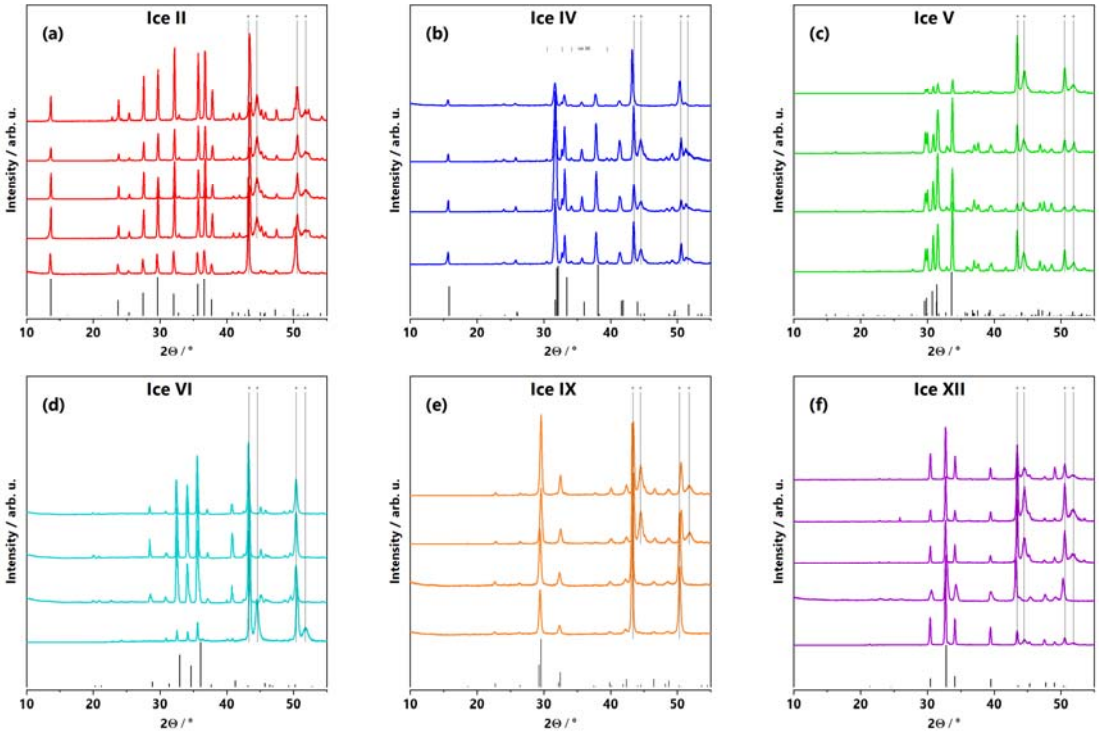

Figure S2: Optical microscope image of a powdered ice sample (ice I_h) at 248 K. The photograph shows the typical size range of grains in powdered ice samples used in the present NIR study (15 to 40 µm for single grains and up to 350 µm for larger grain aggregates).

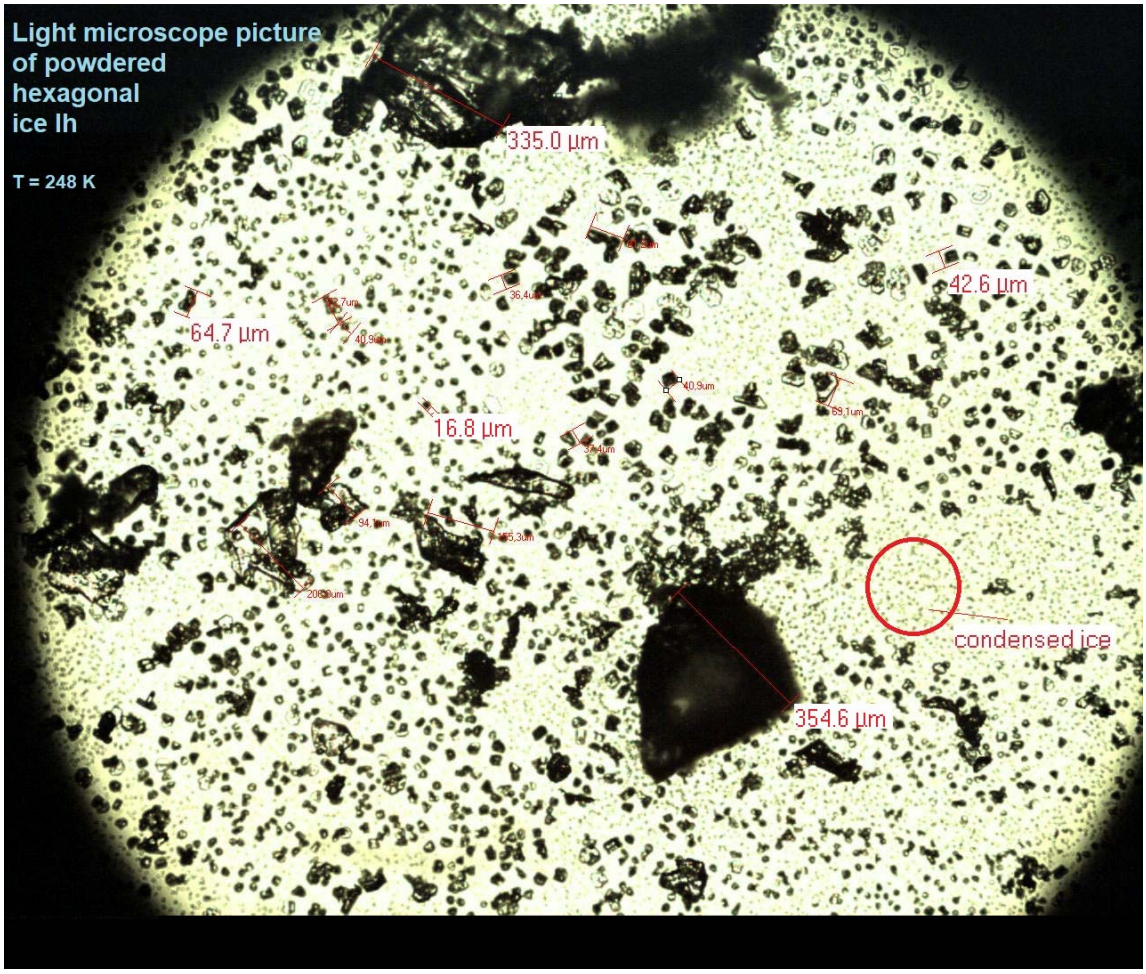

Fig. S3: Depiction of the baseline correction procedure used in the present study for all raw spectra. A basis spline function was constructed from 8 anchor points (purple circles) and then subtracted from the raw spectrum.

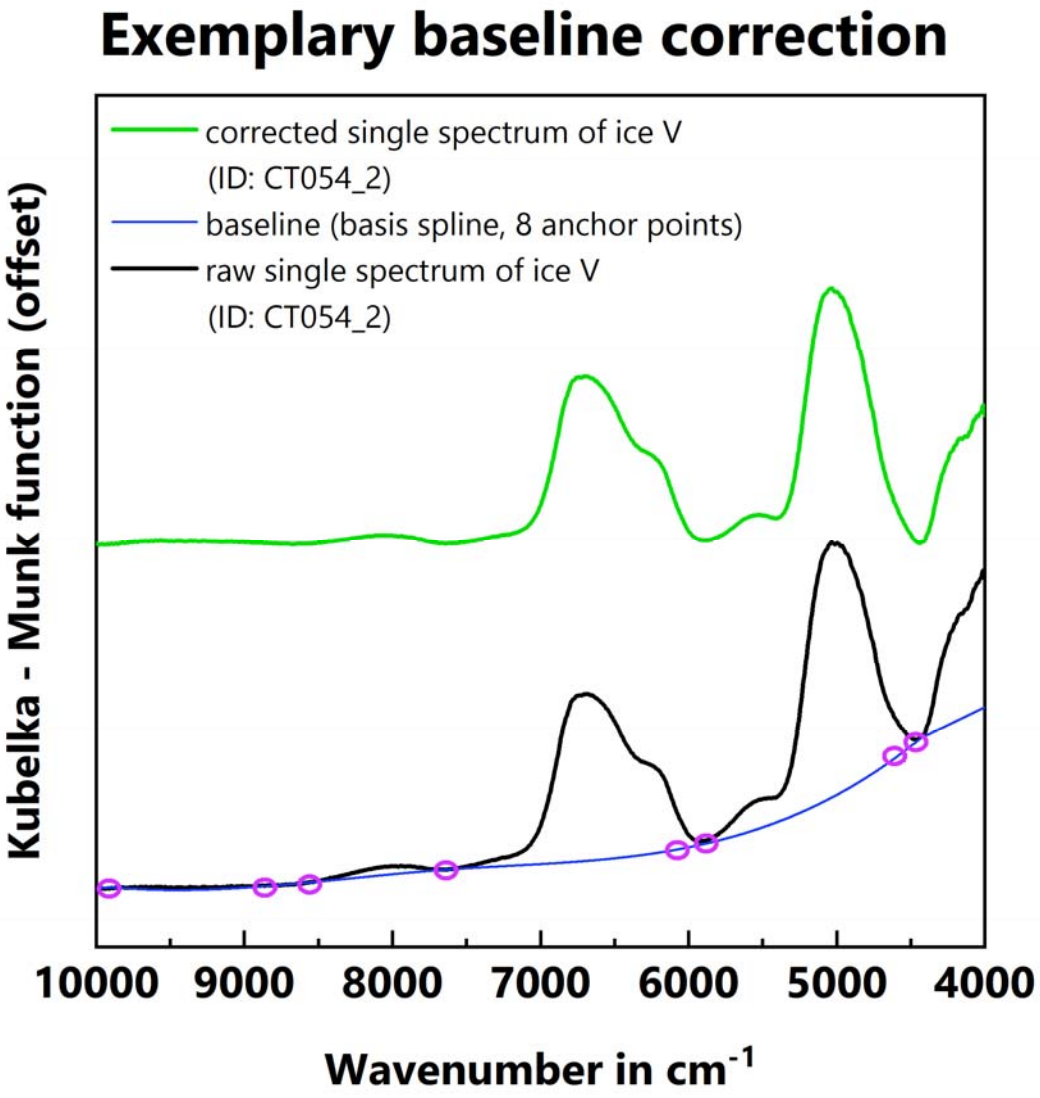

Fig. S4: Identification of peak centres and shoulders using first and second derivative spectra of the K-M function spectra (shown for ice V): For locating the peak centre of the K-M function the zero crossings of the first derivative were considered. Shoulders were identified through minima in the first derivative and zero crossings in the second derivative spectrum.

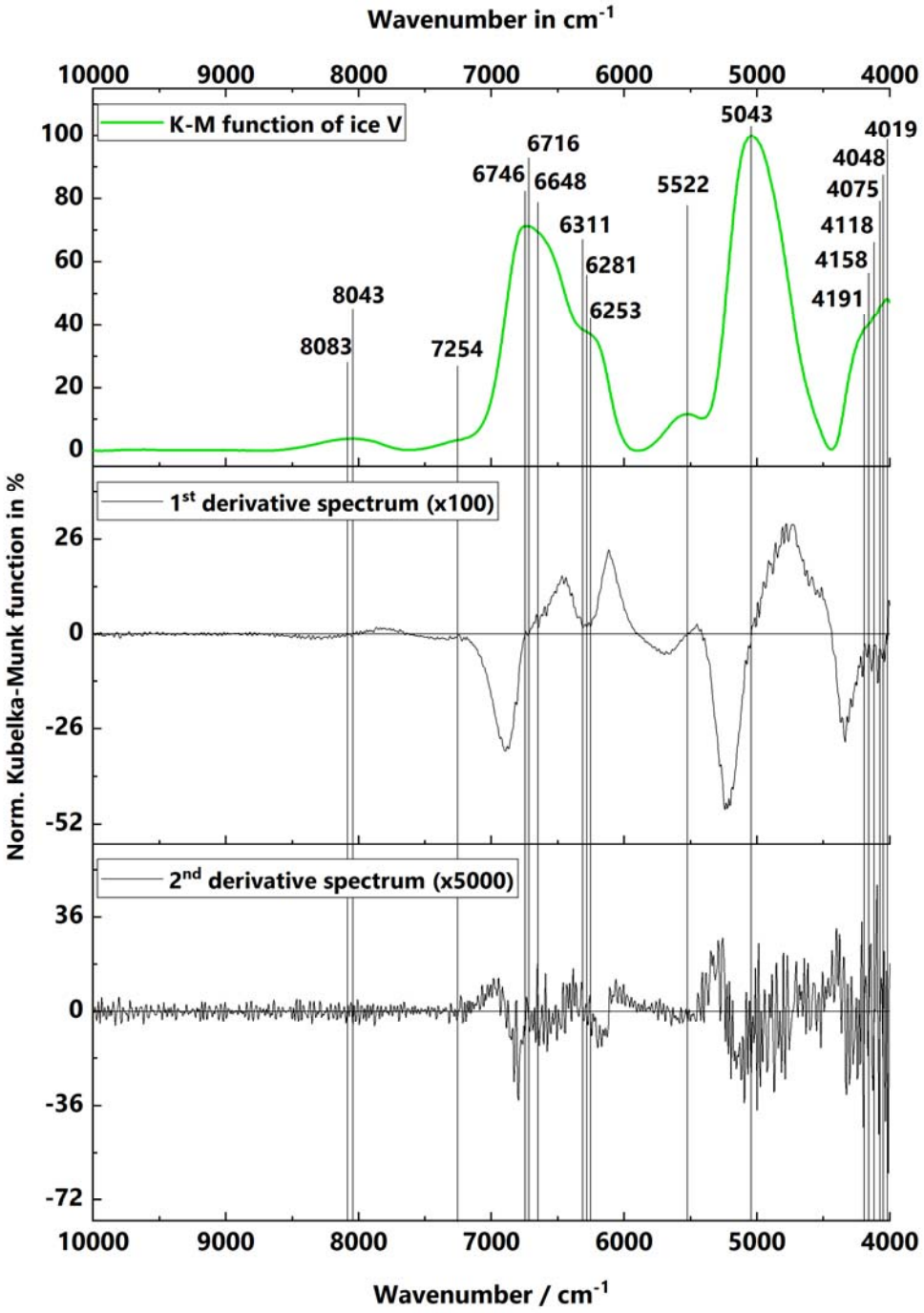

Table S1: Normalized Kubelka-Munk function in % for ices I_h, II, IV, V, VI, IX and XII shown in Fig 1 and Fig 2(ab)

File name: S Table 1.txt

Tables S2-S8: Raw Kubelka-Munk function spectra for ices I_h, II, IV, V, VI, IX and XII

File names: S Table 2_Ih raw.txt

S Table 3_II raw.txt

S Table 4_IX raw.txt

S Table 5_IV raw.txt

S Table 6_V raw.txt

S Table 7_VI raw.txt

S Table 8_XII raw.txt